**REMARKS**

Claims 1, 4-8, 10-18, 21-23, 25-27, and 29-34 are pending in the application. Claims 8, 17, 25 and 31 have been cancelled by this amendment. Therefore, claims 1, 4-7, 10-16, 18, 21-23, 26, 27, 29, 30, and 32-34 are at issue.

The courteous interview granted by Examiner Cheung to applicants' undersigned attorney and Jürgen Schroeder of BASF on June 12, 2007 is hereby acknowledged with appreciation. During the interview, the claims, the Office Action, the cited references, and proposed claim amendments were discussed in detail.

Claims 25 and 31 have been cancelled without prejudice as being directed to non-elected subject matter, as opposed to reasons related to patentability. Applicants reserve the right to file a divisional application directed to the subject matter of claims 25 and 31.

Claims 1, 4-8, 10-18, 21-23, 26, 27, 29, 30, and 32-34 stand rejected under 35 U.S.C. §112, second paragraph, as being indefinite because terms such as "p1+p2+p3" are considered unclear. In response, claims 1, 4, 14, 18, and 21 have been amended to recite "a sum of p1+p2+p3", for example. This amendment is supported in Example 1 at pages 43 and 44 of the specification, wherein the total *sum* of the EO (ethylene oxide) and PO (propylene oxide) units is 3 to 5. Also see specification, page 7, lines 4-8, for further support.

This amendment was discussed at the interview, and the examiner agreed that this amendment would clarify the claims, and overcome the objection. Accordingly, it is submitted that the rejection of the claims under 35 U.S.C. §112, second paragraph, has been overcome and should be withdrawn.

Claims 1 and 4-6 stand rejected under 35 U.S.C. §102(b) as being anticipated by EP 0 777 287 (EP '287) based on the contention that the abstract of EP '287 discloses the ester F of claim 1. Applicants traverse this rejection.

The EP '287 rejection is based on formula (2), i.e., the only glycerin-based compound of EP '287, having a formula:

$$\begin{array}{l} CH_2\text{—}(EO_mPO_n)COCH{=}CH_2 \\ | \\ CH\text{—}(EO_mPO_n)COCH{=}CH_2 \\ | \\ CH_2\text{—}(EO_mPO_n)COCH{=}CH_2 \end{array}$$

wherein m and n do not represent 0 at the same time and $0 \leq n$ and $0 \leq m$ (EP '287, page 4, line 32). Accordingly either EO *or* PO can be absent from the compound, and *no* "upper limit" exists for m, n, or the sum of m+n.

In the examples of EP '287, the sole example directed to a glycerin-based compound is Embodiment 4, wherein n=8 and m=0, illustrated as compound (7) at page 8 of EP '287. This compound is *free* of PO units and contains a sum of *24* EO units.

Present claims 1 and 4-6 are directed to an ester F that *requires* the presence of PO *and* EO units in *each* of the three alkylene oxide chains of the claimed glycerin compound. In addition, total number of EO and PO units in a claimed ester F (not in each alkylene oxide chain) is 3, 4, or 5, as recited. It is submitted, therefore, that even though the very general, broad teachings of EP '287 can read on a presently claimed ester F, EP '287 does not anticipate claims 1 and 4-6 under 35 U.S.C. §102(b).

With respect to a rejection under 35 U.S.C. §102(b), MPEP §2131 states:

> "TO ANTICIPATE A CLAIM, THE REFERENCE MUST TEACH EVERY ELEMENT OF THE CLAIM
>
> 'A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference.' *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987)...'The identical invention must be shown in as complete detail as is contained in the ... claim.' *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). The elements must be arranged as required by the claim, but this is not an *ipsissimis verbis* test, i.e., identity of terminology is not required. *In re Bond*, 910 F.2d 831, 15 USPQ2d 1566 (Fed. Cir. 1990)."

In addition, MPEP §2131.03 II. states:

> "PRIOR ART WHICH TEACHES A RANGE WITHIN, OVERLAPPING, OR TOUCHING THE CLAIMED RANGE ANTICIPATES IF THE PRIOR ART RANGE DISCLOSES THE CLAIMED RANGE WITH "SUFFICIENT SPECIFICITY"
>
> When the prior art discloses a range which touches, overlaps or is within the claimed range, but no specific examples falling within the claimed range are disclosed, a case by case determination must be made as to anticipation. In order to anticipate the claims, the claimed subject matter must be disclosed in the reference with "sufficient specificity to constitute an anticipation under the statute." What constitutes a "sufficient specificity" is fact dependent. If the claims are directed to a narrow range, the reference teaches a broad range, depending on the other facts of the case, it may be reasonable to conclude that the narrow range is not disclosed with "sufficient specificity" to constitute an anticipation of the claims. The unexpected results may also render the claims unobvious. The question of "sufficient specificity" is similar to that of "clearly envisaging" a species from a generic teaching. See MPEP § 2131.02. A 35 U.S.C. 102/ 103 combination rejection is permitted if it is unclear if the reference teaches the range with "sufficient specificity." The examiner must, in this case, provide reasons for anticipation as well as a motivational statement regarding obviousness. *Ex parte Lee*, 31 USPQ2d 1105 (Bd. Pat. App. & Inter. 1993) (expanded Board). For a discussion of the obviousness of ranges see MPEP § 2144.05."

Two recent CAFC decisions support the reasoning stated in MPEP §2131.03 II. In *Eli Lilly & Co. v. Zenith Goldline Pharm. Inc.*, 81 U.S.P.Q. 2d, 1324 (Fed. Cir. 2006), the court stated that for a reference to anticipate a claim, the reference must expressly spell out a definite and limited class of compounds that enable a person skilled in the art to at once envisage each member of this limited class.

In *Impax Labs, Inc. v. Aventis Pharma Inc.*, 468 F.3d 1366 (Fed Circ. 2006), the court stated that the prior art patent disclosed such a large number of compounds that one of ordinary skill in the art would not have recognized that the claimed compound was useful to treat a disease without additional details or guidance, which was not found in the prior art patent.

For the reasons set forth herein, it is submitted that EP '287 fails to anticipate present claims 1 and 4-6 under 35 U.S.C. §102(b), and that claims 1 and 4-6 would not have been obvious over EP '287 under 35 U.S.C. §103.

EP '287 discloses an infinite number of compounds because no upper limit is placed in either variable "m" or "n". In addition, either "m" or "n", but not both, can be zero. The reference therefore fails to disclose the compounds therein with any specificity. Obviously, the general teachings of EP '287 are to a broad a range of compounds, including both glycerin-based compounds and trimethylolpropane-based compounds.

The *sole* specific example of EP '287 directed to glycerin-based compounds is compound (7) which contains 24 EO groups and no PO groups. Accordingly, EP '287 fails to disclose any specific examples within the claimed range, i.e., a glycerin-based compound containing *both* EO and PO groups, wherein the sum of EO and PO is in the claimed narrow range of 3 to 5.

As set forth in the MPEP §2131, the present claims are directed to a narrow range within the wide range of the reference, and wherein the reference fails to disclose a specific example within the claimed range. It is submitted therefore that EP '287 fails to disclose the claimed subject matter with sufficient specificity to constitute an anticipation under 35 U.S.C. §102(b).

To further demonstrate the EP '287 fails to anticipate claims 1 and 4-6, and that EP '287 fails to render those claims obvious under 35 U.S.C. §103, the presently claimed esters exhibit unexpected benefits in the preparation of superabsorbent polymers (SAPs).

In the present specification, Table 1 at page 51 includes seven esters (a through g) that are used as crosslinkers in the preparation of a superabsorbent polymer (SAP). Examples f and g are comparative in that they (a) are based on trimethylolpropane (TMP), (b) contain only EO units, and (c) contain more than a total of 5 EO and PO groups, i.e., Example g. Examples c-e are esters of the present claim 1, i.e., based on glycerin, contain EO *and* PO units, and contain a total of up to 5 PO and EO units. Comparative Example g is the most similar example to the EP '287 disclosure, i.e., based on TMP, containing only EO

units, and containing 15 EO units. See Embodiment 1 of EP '287, based on TMP and containing 18 EO units and no PO units. The only embodiment of EP '287 based on glycerin contains *only* EO and the total number of EO units is 24.

The data in Table 2 of the specification shows that claimed esters c-e provide an SAP having a very low crosslinker residue (over replicate tests) of from less than 5 to 10 ppm. In contrast, a crosslinker based on TMP and containing 15 EO units (i.e., g) provided in SAP having 20 to 51 ppm crosslinker residue. A comparative crosslinker based on TMP and containing 3 EO units provided on SAP having 857 to 1302 ppm of residual crosslinkers.

In addition, the claimed esters c-e provided SAPs having a VSI value (saponification index) of 7.5 to 9.5. Comparative TMP-based esters f and g demonstrated a VSI value of 36.9 and 11.6, respectively.

The presently claimed esters therefore show unexpected results with respect to crosslinker residue, which ideally is zero to avoid free monomers in the resulting SAP or the need to perform a method step to remove the crosslinker residue. Unexpected results also are demonstrated with respect to VSI values. As stated in the specification, an ideal crosslinker has a VSI of zero because then all crosslinking is performed during the reaction, as opposed to during a drying step. In turn, the properties of the SAP are not altered by the drying process. See specification, page 50, lines 1-6.

In view of the broad disclosure of the EP '287, including trimethylolpropane and glycerin-based triacrylates, that the disclosed compounds can be free of either EO or PO units, that the number of disclosed compounds is infinite (i.e., m $\leq$0 and n $\leq$0), that the examples are primarily directed to TMP-based compounds, and that the only glycerin-based example contains 24 EO units only, it is submitted that EP '287 cannot anticipate claims 1 and 4-6 under 35 U.S.C. §102 (b) or render claims 1 and 4-6 obvious under 35 U.S.C. §103.

The present claims are closely tailored to be based on glycerin, contain EO *and* PO units, and contain a total *sum* of EO and PO units of 3, 4, or 5, wherein the esters demonstrate unexpected results with respect to performing as a crosslinking agent for an

SAP. EP '287 fails to disclose the presently claimed esters with any specificity. EP '287 also provides no direction, guidance, or apparent reason for a person skilled in the art of SAPs to select the narrow range of claimed compounds from the infinite number of compounds in the reference (which is directed to a non-aqueous electrolyte secondary battery) with any reasonable expectation of providing a crosslinker for SAPs having unexpectedly improved properties over SAPs crosslinked with other esters also broadly disclosed in EP '287 and closer in structure to the examples of EP '287.

For all of the reasons set forth above, it is submitted that claims 1 and 4-6 are not anticipated under 35 U.S.C. §102(b) by EP '287 and that the rejection should be withdrawn. It is further submitted that claims 1 and 4-6 would not have been obvious to a person skilled in the art under 35 U.S.C. §103.

Claims 7, 8, and 10 stand rejected under 35 U.S.C. §102(b) as being anticipated by Barthold et al. U.S. Patent No. 5,472,617 ('617). The examiner bases this rejection as the contention that the '617 patent purportedly discloses stripping with a gas which is inert under the reaction conditions. Applicants traverse this rejection.

First, please note that claim 7 has been amended to incorporate the features of claim 8, i.e., a process for preparing an ester F in the presence of a molar excess of (meth)acrylic acid to alkoxylated glycol of at least 3.15:1. The '617 patent specifically teaches that a molar excess of (meth)acrylic acid should be *avoided*. See '617 patent, column 4, line 63 through column 5, line 1.

With respect to the claimed feature of stripping with a gas, at column 10, line 52 through column 11, line 2, the '617 patent discloses reacting an alkoxylated alcohol with acrylic acid "under a nitrogen blanket". This is not equivalent to the stripping step i) recited in claim 7. Note that the nitrogen blanket in the '617 patent is applied *during* the reaction between the alkoxylated alcohol and the acrylic acid. The disclosed "nitrogen blanket" is not a stripping function, but, as well known in the art, is applied over a reaction mixture in the '617 patent to *preclude* the introduction of oxygen into the reaction system.

The presently claimed stripping step i) is performed *after* the reaction between the alkoxylated glycol and the (meth)acrylic acid to form the ester F. The '617 patent teaches a nitrogen blanket over a reaction utilizing alkoxylated trimethylolpropane, which alone is a difference that precludes a rejection under 35 U.S.C. §102(b). The fact that the '617 patent teaches a nitrogen blanket during polymerization, rather than stripping *after* polymerization is another difference between claim 7 and the '617 patent disclosure.

A major difference between claim 7 and the '617 patent is that "stripping" is different from a "nitrogen blanket". Attached hereto as Exhibit A from *Hawley's Condensed Chemical Dictionary, Thirteen Ed.* (1997), page 1052, is a definition of "stripping" showing that the term refers to the removal of volatile components from a liquid mixture by the passage of a gas through the liquid mixture. This stripping removes a solvent from the reaction mixture *after* the polymerization.

Still another major difference between the '617 patent and claim 7 is that the stripping is performed using an "oxygen-containing gas", as presently recited in amended claim 7. This amendment is supported by the present specification at page 22, lines 34-36. An oxygen-containing gas is utilized in the stripping step to maintain the inhibitory capabilities of a compound like MEHQ during solvent removal, i.e., to inhibit premature polymerization of the formed ester F. It is well-known in the art that oxygen must be present to maintain this polymerization inhibitory capability. See Exhibit B submitted concurrently with this amendment, an excerpt from "Modern Superabsorbent Polymer Technology" (1998), page 39-44, showing the influence of oxygen on polymerization inhibition.

The '617 patent utilizes a nitrogen blanket to help *remove* oxygen from the reaction system, such that the inhibition capabilities of MEHQ are reduced and the polymerization can proceed. Accordingly, the "nitrogen blanket" of the '617 patent and the "stripping" step are not identical (e.g., are performed at different steps of the reaction and perform different functions), and the '617 patent differs from claims 7 and 10 such that a rejection under 35 U.S.C. 102(b) cannot be sustained.

Finally, the '617 patent fails to teach or suggest a mole excess of at least 3:15:1 of (meth)acrylic acid in the reaction mixture. The '617 patent fails to consider or address

using such mole excess of (meth)acrylic acid, and provides no apparent reason for a person skilled in the art to use such a molar excess of (meth)acrylic acid. In contrast, the '617 patent, at column 4, line 63 through column 5, line 1, specifically teaches a 1:1 molar ratio (per hydroxyl group of the alcohol) of oxyalkylated alcohol to (meth)acrylic acid, and that an excess of (meth)acrylic acid should be avoided.

Therefore, claims 7 and 10 would not have been obvious under 35 U.S.C. §103 over the '617 patent. The '617 patent fails to teach or suggest a solvent stripping step, using an excess molar amount of (meth)acrylic acid, *and* fails to provide any apparent reason for performing such steps. In summary, process claims 7 and 10 are patentable over the cited '617 patent, and the rejection should be withdrawn.

Claims 11-13, which depend from claim 7, also stand rejected under 35 U.S.C. §103 as being obvious over the '617 patent. For the reasons set forth above, it is submitted that claims 11-13 also are patentable over the '617 patent for same of the reasons that claims 7 and 10 are patentable over the cited '617 patent.

In addition, the examiner has failed to articulate why claims 11-13 would have been obvious over the '617 patent, except for a conclusory statement relating to "routine experimentation". In particular, the examiner is directed to the recent *KSR Int'l Co. v. Teleflex*, ---U.S.---, No. 04-1350 (U.S. Apr. 30, 2007) decision. The mandate of the United State Supreme Court in this decision is that the Patent Office *must* make it clear in the record that the teaching-suggestion-motivation to modify the reference exists. As emphasized by the Supreme Court, "rejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR Int'l Co. v. Teleflex, Inc.*, ---U.S.---, No. 04-1350, slip op. at 14 (April 30, 2007).

The *KSR* decision also was the subject of a May 3, 2007 memorandum from the Deputy Commissioner for Patent Operations, which stated at page 2 (emphasis in original):

"(4) The Court noted that the analysis supporting a rejection under 35 U.S.C. § 103(a) should be made explicit, and that it was "important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the [prior art] elements" in the manner claimed. The Court specifically stated:

> Often, it will be necessary...to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was an **apparent reason** to combine the known elements in the fashion claimed by the patent at issue. To facilitate review, this analysis **should be made explicit**.

*KSR*, slip op. at 14 (emphasis added).

**Therefore, in formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements, it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed.**"

Also note that claim 13 recites a molar ratio of (meth)acrylic acid to alkoxylated glycerol in step a) of at least 15:1. The '617 patent absolutely fails to teach, suggest, or even consider such a mole excess of (meth)acrylic acid in the reaction mixture, as stated above.

It is submitted, therefore, that the present rejection does not provide any articulated reasoning to support a conclusion of obviousness of claims 11-13 over the '617 patent, and that this rejection should be withdrawn.

Claims 14-17 stand rejected under 35 U.S.C. §102(b) as being anticipated by the '617 patent. Applicants traverse this rejection.

Claim 17 has been cancelled. Therefore, this rejection is moot as to claim 7.

Claim 16 depends from claim 7, and is patentable for the reasons set forth above with respect to the rejection of claims 7 and 10 over the '617 patent.

With respect to claims 14 and 15, each claim, as amended, recites a postcrosslinking step and a drying step. The '617 patent fails to disclose either of these steps, let alone both. Accordingly, differences exist between claims 14 and 15 and the '617 patent, such that a rejection under 35 U.S.C. §102(b) cannot be maintained. It is further submitted that the differences are nonobvious differences. In particular, the '617 patent fails to teach a postcrosslinking step or a drying step, and provides no apparent reason for a person skilled in the art to perform such steps. It must be noted that an SAP is postcrosslinked to improve fluid absorption properties. The polymers of the '617 are not SAPs, but oil demulsifiers. Thus, an improvement of fluid absorption properties is neither considered nor addressed by the '617 patent. In summary, claims 14 and 15 are patentable over the '617 patent.

Claims 18 and 21-23 stand rejected under 35 U.S.C. §102(b) as being anticipated by the '617 patent. Applicant traverses this rejection. The patentable differences between claim 21 relating to ester F of claim 1 and the '617 patent has been discussed above.

With respect to ester F of formula Ia of claim 18, the '617 patent specifically discloses a ratio of alcohol to alkoxides of from 1:120 to 1:5. See '617 patent at column 3, lines 64 and 65. Claims 18 and 21 have been amended to recite a sum of p1 + p2 + p3 is 3 or 4. Accordingly, a difference exists between the '617 patent and present claims 18 and 21-23 such that a rejection under 35 U.S.C. §102(b) cannot be maintained.

In addition, the differences between claims 18 and 21-23 and the '617 patent are nonobvious differences. The '617 patent generally teaches monofunctional and multifunctional alcohols at column 3, lines 36-53. Glycerol is disclosed among more than specific 20 alcohols. The '617 patent also discloses 15 alkoxylated alcohols at Table 1 of the reference. No disclosed alkoxylated alcohol in the examples is glycerin, and the ratio of alcohol to alkylene oxide is far above the ratio of 1 to 3 and 1 to 4 recited in claims 16 and 21, e.g., Example a3 of the '617 patent has a ratio of 1 to about 40, Example a4 has a ratio of 1 to about 36. Example a5 has a ratio of 1 to about 66, and Example a6 is 1 to about 40.

The specific teachings of the '617 patent therefore are directed to alkoxylated alcohols containing a high amount of alkylene oxide. Persons skilled in the art, after reading the '617 patent, would have had no apparent reason to select glycerin from the long list of disclosed alcohols, then alkoxylate with only 3 or 4 ethylene oxide and/or propylene oxide units. Accordingly, it is submitted that claims 18 and 21-23 would not have been obvious to a person of ordinary skill in the art in view of the '617 patent.

With respect to the examiner's contentions regarding the term "diluent" in claim 22, claim 10 of the '617 patent refers to an oil/water mixture to which the copolymer is added to *effect* demulsification. The "crude oil and water mixture" is *not* present in the composition prior to polymerization as recited in claim 21, but is present after polymerization. See '617 patent, column 8, lines 40-61. To clarify claim 22, the claim has been amended to recite that the diluent is water and/or a water-soluble organic solvent. Support for the amendment to claim 22 can be found in the specification at page 19, lines 13-21.

With respect to the examiner's comments regarding the '617 patent at column 1, lines 52-62, this portion of the '617 specification is directed to *prior* resins that demonstrates *disadvantages*, such as gelling. The '617 patent disclosure is not directed to the resins disclosed at column 1, lines 52-62, but to resins that may overcome these disadvantages. The '617 patent therefore is directed to resins that do *not* gel, in contrast to the presently claimed SAPs.

In summary, differences exist between the '617 patent and claims 18 and 21-23 such that the rejection under 35 U.S.C. §102(b) cannot be maintained. In addition, in view of the amendments to claims 18, 21, and 22, it is submitted that claims 18 and 21-23 would not have been obvious over the '617 patent under 35 U.S.C. §103.

Claims 26, 27, 29, 30 and 32-34 stand rejected under 35 U.S.C. §102(b) as being anticipated by, and alternatively under 35 U.S.C. §103 as being obvious over, the '617 patent. Applicants traverse this rejection.

Claims 26 and 27 have been amended to depend from claim 14, in view of the cancellation of claim 17.

All the examiner's contentions supporting this rejection have been addressed above, e.g., gels and "diluents", and it is submitted that claims 26, 27, 29, 30, and 32-34 are patentable over the '617 patent for the same reasons claims 7, 10-16, 18, and 21-23 are patentable over this reference under both 35 U.S.C. §102(b) and 103, and that this rejection should be withdrawn.

All pending claims are in a form and scope for allowance. An early and favorable action on the merits is respectfully requested.

Should the examiner wish to discuss the foregoing, or any matter of form in an effort to advance this application toward allowance, the examiner is urged to telephone the undersigned at the indicated number.

Dated: August 1, 2007

Respectfully submitted,

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Exhibit A

# *Hawley's*

# *Condensed Chemical*

# *Dictionary*

*THIRTEENTH EDITION*

*Revised by*

Richard J. Lewis, Sr.

VAN NOSTRAND REINHOLD

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from *Streptomyces flocculus*. Dark-brown, rectangular crystals.

**stress.** The deformation undergone by a material when subjected to a definite load (the force applied per unit area). The load may be static (constant) or dynamic (increasing at a uniform rate). In either case it induces a strain in the material that results in rupture if the deforming force exceeds its strength.
See strain; modulus of elasticity.

**stress cracking.** (tension cracking). Development of transverse cracks in a rubber or plastic product exposed to atmospheric oxygen at low (5–10%) elongation for long periods of time, for example, coiled hose, packaging materials, etc., both in service and during storage. Cracking will occur in the absence of light. It can be minimized in the case of a plastic such as polyethylene by lowering the density and the melt index, and in rubber by use of antioxidants.

**stripping.** (1) Removal of relatively volatile components from a gasoline or other liquid mixture by distillation, evaporation, or by passage of steam, air, or other gas through the liquid mixture. (2) Rapid removal of color from an improperly dyed fabric or fiber by a chemical reaction. Compounds used for this purpose in vat dyeing or in discharge printing are termed *discharging agents*. Substances commonly used as strippers are sodium hydrosulfite, titanous sulfate, sodium and zinc formaldehyde sulfoxylates.

**strontia.** See strontium oxide.

**strontianite.** $SrCO_3$. Natural strontium carbonate.
**Properties:** White, gray, yellow, green color; vitreous luster. Mohs hardness 3.5–4, d 3.7.
**Occurrence:** California, New York, Washington, Germany, Mexico.
**Use:** Source of strontium chemicals.

**strontium.** Sr. Metallic element of atomic number 38, group IIA of periodic table, aw 87.62, valence = 2, radioactive isotopes strontium-89 and strontium-90. There are four stable isotopes.
**Properties:** Pale-yellow, soft metal; chemically similar to calcium. D 2.54, mp 752, bp 1390C. Soluble in alcohol and acids; decomposes water on contact.
**Occurrence:** Ores of strontianite and celestite (Mexico, Spain).
**Derivation:** (1) Electrolysis of molten strontium chloride in a graphite crucible with cooling of the upper, cathodic space; (2) thermal reduction of the oxide with metallic aluminum (strontium aluminum alloy formed), and distilling the strontium in a vacuum.
**Grade:** Technical.
**Hazard:** Spontaneously flammable in powder form, ignites when heated above its mp. Reacts with water to evolve hydrogen. Store under naphtha.
**Use:** Alloys, "getter" in electron tubes.

**strontium-90.** Radioactive strontium isotope.
**Properties:** Half-life is 38 years. Radiation: $\beta$.
**Derivation:** From the fission products of nuclear reactor fuels.
**Available forms:** A mixture containing strontium-90, yttrium-90, and strontium-89 chlorides in hydrochloric acid solution; also as the carbonate and titanate.
**Hazard:** Highly toxic radioactive poison; present in fallout from nuclear explosions. Absorbed by growing plants; when ingested attacks bone marrow with possibly fatal results. It may be partially removed from milk by treatment with vermiculite.
**Use:** Radiation source in industrial thickness gauges, elimination of static charge, treatment of eye diseases, in radio-autography to determine the uniformity of material distribution, in electronics for studying strontium oxide in vacuum tubes, activation of phosphors, source of ionizing radiation in luminous paint, cigarette density control, measuring silk density, atomic batteries, etc.

**strontium acetate.**
CAS: 543-94-2. $Sr(C_2H_3O_2)_2 \cdot 1/2H_2O$.
**Properties:** White, crystalline powder. Soluble in water; loses $1/2H_2O$ at 150C.
**Derivation:** Interaction of strontium hydroxide and acetic acid, followed by crystallization.
**Use:** Intermediate for strontium compounds, catalyst production.

**strontium bromate.** $Sr(BrO_3)_2 \cdot H_2O$.
**Properties:** Colorless or yellowish crystals, lustrous powder, hygroscopic. D 3.773, loses water at 120C, decomposes at 240C. Soluble in water.
**Hazard:** Strong oxidant, fire risk in contact with organic materials.

**strontium bromide.**
CAS: 10476-81-0. $SrBr_2 \cdot 6H_2O$.
**Properties:** White, hygroscopic crystals or powder. D 2.386 (25/4C), loses $4H_2O$ at 89C, losing remaining water by 180C; mp (anhydrous salt) 643C. Soluble in water, alcohol, and amyl alcohol; insoluble in ether.
**Derivation:** Strontium carbonate is treated with bromine or hydrobromic acid.
**Grade:** Anhydrous powder, crystals, technical, CP.
**Hazard:** Toxic by ingestion and inhalation.
**Use:** Medicine (sedative), lab reagent.

**strontium carbonate.** $SrCO_3$.
**Properties:** White, impalpable powder. D 3.62, loses carbon dioxide at 1340C. Soluble in acids, carbonated water, and solutions of ammonium salts; slightly soluble in water.

Exhibit B

# MODERN SUPERABSORBENT POLYMER TECHNOLOGY

Edited by

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**Table 2.4. Comparison of polymerization rate measurements**

| Reference | T(°C) | pH | $[M]_0$ | Initiator type[a] | $[I]_0$ | $R_p/[M]^{3/2}[I]^{1/2}$ |
|---|---|---|---|---|---|---|
| Manickam et al.[38] | 50 | 1 | 0.138 | KPS | 0.01 | 0.491–0.586 |
| | 50 | 4.2 | 0.172 | KPS | 0.01 | 0.236 |
| | 50 | 11 | 0.258 | KPS | 0.01 | 0.091–0.444 |
| Kabanov et al.[32] | 60 | 1 | 1.2 | AIBN | 0.005 | 0.14 |
| | 60 | 10 | 1.2 | AIBN | 0.005 | 0.19 |
| | 60 | ~7 | 1.2 | AIBN | 0.005 | 0.00278 |
| Ito et al.[31] | 50 | 2.4 | 0.5 | APS | 0.00285 | 0.90 |
| | 50 | 4.7 | 0.5 | APS | 0.00285 | 0.14 |
| | 50 | 7.2 | 0.5 | APS | 0.00285 | 0.045 |
| Cutié et al.[24] | 55 | 4.5 | 1.14–4.56 | NPS | 0.0023 | 0.126–0.239 |

[a]KPS, potassium persulfate; AIBN, 2,2′-azobis(isobutyronitrile); APS, ammonium persulfate; NPS, sodium persulfate.

cation for a batch polymerization is that the molecular weight will likely decrease as the polymerization proceeds, because the rate of propagation decreases while termination and initiation remain relatively constant. In Figure 2.9 the cumulative molecular weight data from identical isothermal polymerizations at 55°C are plotted versus the extent of conversion, illustrating this point.[36] Two notes should be made of these data: (1) The molecular weight decreases significantly with conversion, which, while anticipated, confirms the likelihood of forming a low-molecular-weight fraction late in the polymerization; and (2) the molecular weight values are large compared with those for many other polymers. The unusually large molecular weight of many commercial acrylic acid (and acrylamide) polymers is utilized in the application of the soluble (uncrosslinked) polymers as viscosifiers and flocculants.[40] This is probably a reflection of their high propagation rates, compared with those for other monomers, rather than low termination or initiation rates. For example, from a comparison of chemical structures one might expect the polymerization of acrylic acid to proceed at a rate similar to that for methylacrylate. In fact, at 60°C the propagation of aqueous acrylic acid, as determined from rotating sector experiments,[41] is faster than that of methylacrylate.[26] Results of Laborie[42] and of Chapiro and Dulieu[43] suggest that the high value for the propagation rate results from an interesting templating effect at high concentrations due to hydrogen bonding with water. In aprotic solvents, without such hydrogen bonding, the rates are much lower.

### 2.5.3. Inhibition

As noted in section 2.2.2.1, commercial monomer grade acrylic acid typically contains 200 ppm MEHQ, and it is recommended that it be stored under an air atmosphere. This is a high level of inhibitor when compared with that used in other vinyl

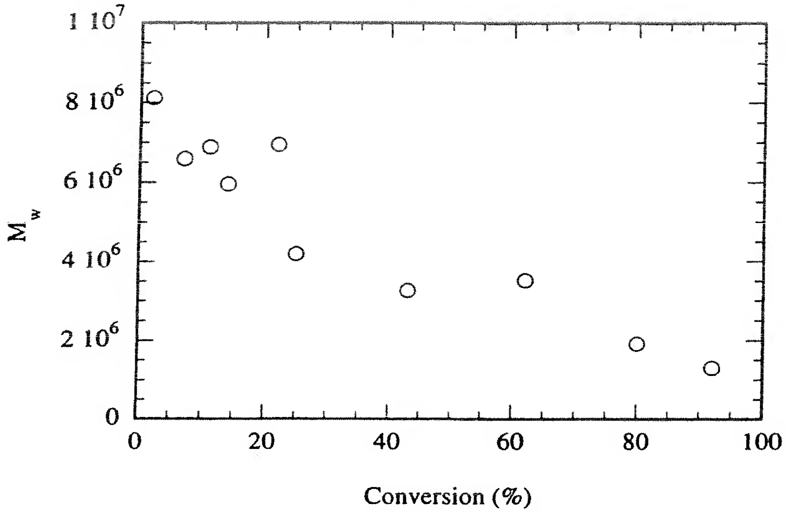


**Figure 2.9.** Effect of conversion on cumulative molecular weight ($M_w$). Polymerization was at 65% neutralization and 55°C.

monomers. Styrene, for example, is inhibited with 3–10 ppm of *tert*-butylcatechol. Reproducible polymerizations of acrylic acid generally begin with the deoxygenation of the system, and induction times vary roughly inversely with oxygen concentration.

The role of oxygen in the stability of vinyl monomers is complicated. For example, most purified vinyl monomers will not polymerize upon heating in the absence of oxygen (styrene being an exception), but virtually all vinyl monomers will readily form peroxides upon exposure to air. These peroxides have been found to break down and initiate polymerization at elevated temperatures.[44] At lower temperatures, where the peroxides are relatively stable, oxygen often reacts with other free radicals in the system, thereby functioning as an inhibitor. This delicate balance between inhibition and reinitiation is influenced by temperature, the oxygen content of the system, and the thermal stability of the peroxide formed from the particular monomer. In a closed system, oxygen is eventually depleted and polymerization proceeds. In contrast, when there is an unlimited supply of oxygen, such as in an open vessel, vinyl monomers will absorb a large quantity of oxygen, forming polyperoxides but not polymerizing.[45]

Even trace amounts of oxygen in otherwise very pure systems can suppress the polymerization of acrylic or methacrylic acids. Blauer[46] reported that even the small amounts of oxygen remaining in *purified* nitrogen would retard the polymerization of methacrylic acid if continuously bubbled through the solution during the reaction. Levy[47] has shown that, in the absence of oxygen, there is no induction time at 100°C for MEHQ-inhibited acrylic acid, and no detectable amount of MEHQ is consumed or reacts with the polymer radicals. By continuously monitoring the oxy-

gen level in the reaction vessel, Kurland[48] determined the oxygen consumption during polymerization of neat acrylic acid at 50°C containing relatively high (106 ppm) and low (1.7 ppm) levels of MEHQ. At the lower level, a rapid increase in the rate of oxygen consumption was observed once the MEHQ was depleted. Initially about six molecules of oxygen were consumed per initiator radical generated, but, when the MEHQ was depleted, about 32 molecules per radical were consumed. Regardless of the MEHQ content, polymerization occurred when the oxygen content was reduced to about 0.5 ppm, clearly showing that the polymerization is inhibited by oxygen, not MEHQ. The rate of oxygen consumption, however, is much slower in the presence of higher levels of MEHQ.

Levels of MEHQ ranging from 16 to 151 ppm have been found in commercial superabsorbent polymers, as indicated in Table 2.5. The amount of MEHQ that survives the polymerization process may be the result of the efficiency of deoxygenation, the reaction temperature, and, most important, the nature of the polymerization catalyst. Persulfates are more powerful oxidants than azo compounds and more efficient at hydrogen abstraction; they may therefore convert more of the MEHQ to quinone.[24,49] The latter has been detected as a byproduct of the MEHQ-inhibited acrylic acid polymerization initiated with sodium persulfate.

The mechanism for inhibition/retardation presented in section 2.4.3 implies that, if the inhibition constant $z$ ($= k_z/k_p$) is large, significant polymerization will not occur until the species $Z$ is completely consumed (induction period), after which time the rate is normal (inhibition). If the effect is milder ($z$ is smaller), polymerization occurs from the outset but at a reduced rate (retardation).[26] MEHQ in acrylic acid may not fit cleanly into either category. In a study of the isothermal persulfate-initiated polymerization of acrylic acid at various MEHQ levels,[24] the initial observations were the following:

1. In deoxygenated runs, polymerization began almost immediately.
2. The rate was lowered by the addition of MEHQ.
3. MEHQ was found in the polymer after essentially complete conversion.

**Table 2.5. Residual MEHQ levels in selected superabsorbent polymer samples from eight manufacturers, over several years**

| Manufacturer Designation | MEHQ Content (ppm) |
|---|---|
| A | 151, 67 |
| B | 109 |
| C | 32, 84 |
| D | 94, 46 |
| E | 46 |
| F | 54, 32 |
| G | 33 |
| H | 30, 34, 16 |

These three factors all indicate that MEHQ behaves like a retarder in this system. In other words, the reaction described in Eq. 2.13 would be significant but would not prevent considerable "normal" polymerization from occurring. Referring to Eq. 2.14, this would be a situation in which the third term $k_z[Z][RM\cdot]$ dominates the second term $2k_t[RM\cdot]^2$ sufficiently to reduce the rate by lowering the radical concentration. This in turn would imply that $[RM\cdot]$, and hence the polymerization rate, would depend on the *first power of initiator concentration*. In addition, one would expect chain termination by a small molecule (Eq. 2.13) to result in half the average molecular weight seen with normal recombination of growing polymer chains.

However, it was found that the rates of polymerization at various levels of MEHQ and persulfate depend approximately on the half power of the initiator, as would be expected for an uninhibited reaction. Furthermore, molecular weights show either little change with increased inhibitor level or actually appear to increase. These deviations from the expected retardation behavior can be accommodated by a novel mechanism described in Eqs. 2.24 and 2.25 (this approach was originally proposed to us by D.J. Arriola of The Dow Chemical Co.) If the radical originating from the initiator fragment $R\cdot$ has a noticeably different reactivity with the inhibitor or the monomer from that of polymer-based radicals, the following reaction scheme should be used:

$$R\cdot + Z \xrightarrow{k_z} inactive \tag{2.24}$$

$$R\cdot + M \xrightarrow{k'} RM\cdot \tag{2.25}$$

The reaction of $RM\cdot$ with $Z$ (Eq. 2.13) does not occur to a significant extent, but the remainder of the polymerization follows the mechanism described in section 2.4.1.

The concentration of the initiator fragment $[R\cdot]$ is still at steady state, as in Eq. 2.26. Rearranging Eq. 2.26 results in an expression for the steady-state concentration of $[R\cdot]$, Eq. 2.27:

$$\frac{d[R\cdot]}{dt} = 2k_d[I] - k_z[R\cdot][Z] - k'[R\cdot][M] = 0 \tag{2.26}$$

$$[R\cdot] = \frac{2k_d[I]}{k_z[Z] + k_i[M]} \tag{2.27}$$

Substituting this expression for the steady-state concentration of initiator radicals into Eq. 2.14 yields Eq. 2.28:

$$[RM\cdot] = \left(\frac{k_d[I]}{k_t}\right)^{1/2}\left(\frac{k_i[M]}{k_z[Z] + k_i[M]}\right)^{1/2} \tag{2.28}$$

By inverting and squaring Eq. 2.28, Eq. 2.29 is obtained:

$$\frac{1}{[RM\cdot]^2} = \frac{k_t}{k_d[I]}\left(1 + \frac{k_z[Z]}{k_i[M]}\right) \tag{2.29}$$

Largely independent of polymerization mechanism, a pseudo-first-order rate constant for a polymerization (i.e., the slope of the ln$[M]$ vs. time curve) is equal to $k_p[RM\cdot]$, as apparent from Eq. 2.5. Different mechanisms primarily affect the value of $[RM\cdot]$. If one had pseudo-first-order rate constants at various inhibitor levels $[Z]$, but at a fixed series of initiator concentrations $[I]$, one could plot $1/(k_p[RM\cdot])^2$ vs. $[Z]$ for each $[I]$ and determine $k_z/k_i$. From experiments at fixed levels of inhibitor and varying, though irregular, levels of initiator, appropriate values of $k_p[RM\cdot]$ were interpolated for fixed initiator concentrations, and the plot described is shown in Figure 2.10. Values of $k_z/k_i$ obtained from this plot are given in Table 2.6.

These values are remarkably constant. They are rather high compared with the values for the inhibition constant $z$ $(= k_z/k_p)$ given by Odian.[26] We should note, however, that $k_i$ in this case is probably significantly smaller than $k_p$. If $k_i$ were equal to or greater than $k_p$, there would be no apparent effect of MEHQ on the kinetics, because nothing would "intercept" the initiator fragment but monomer. Since $k_i$ must be smaller than $k_p$, $k_z/k_i$ would be larger than the value expected for $k_z/k_p$ from Odian's table.[26] This is the case, and thus there is internal consistency. In summary, the data are adequately explained if the MEHQ inhibitor is inferred to primarily intercept the initiator radical rather than the growing polymer radical.

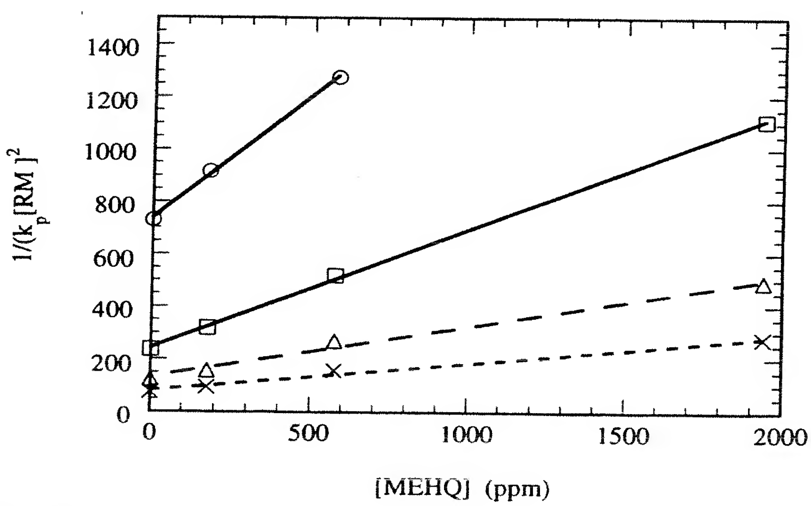


**Figure 2.10.** Dependence of inverse square of $k_p[RM\cdot]$ on the concentration of MEHQ for several values of $[I]$. $[I]$ = 0.0032 (○), 0.0064 (□), 0.010 (△), 0.0144 (x).

**Table 2.6. Calculated values of $k_z/k_i$ for various initiator concentrations**

| Interpolated $[I]$ (mol/L) | $k_z/k_i$ |
|---|---|
| 0.0016 | 2,405 |
| 0.0036 | 3,506 |
| 0.0064 | 2,711 |
| 0.01 | 2,409 |
| 0.0144 | 2,523 |

### 2.5.4. Reactions Near Dryness

***2.5.4.1. Continuation of Polymerization.*** Drying is an essential step in nearly every superabsorbent manufacturing process (see Chapter 3, section 3.2.5). Reactions normally studied in a polymerization reactor often continue during drying operations; events occurring in this regime may be particularly important in determining residual monomer levels in the final product. The impact on residual levels of the breakdown of co-polymerized acrylic acid dimer is discussed in section 2.2.2.2; but in the present section we consider the effect of the continuation of polymerization during drying. Both initiator and moisture levels are changing rapidly and independently of one another during drying, and this situation dramatically affects the polymerization rate of any remaining monomer. As an illustration of this interaction, a patent by Irie et al.[50] claims that the humidity of the drying air must be controlled so that polymer does not dry too quickly, thereby extending the polymerization reaction.

Studies of the rate of decrease in residual monomer concentration using nearly dry (down to 5% moisture) polymer samples held in closed vessels under nitrogen yield results that can be extrapolated from those obtained at reactor conditions. In other words, $R_p$ is dependent on $[M]^{3/2}$ and $[I]^{1/2}$. In fact, at the increased solids content, the residual monomer can be reduced to undetectable levels under nitrogen. Similar studies of monomer reduction in closed systems in an air atmosphere show that oxygen inhibits this last bit of polymerization, as would be expected (S.S. Cutié et al., The Dow Chemical Co., unpublished results).

Very dry samples of sodium polyacrylate, for example, below 5% moisture, show reduced diffusion rates for moisture and oxygen. This can be interpreted as resulting from the transition of the polymer to a glassy state at reduced moisture. An inflection in the heat demand as measured by differential scanning calorimetry has been related to a glass transition temperature $T_g$. (see Chapter 4, section 4.5.2.1). A plot of this inflection temperature versus the weight loss obtained from thermal gravimetric analysis for a series of sodium polyacrylate gel samples is shown in Figure 2.11 (A.J. Pasztor, Jr. et al., The Dow Chemical Co., unpublished results). The effect of the state of the reacting polymer gel, whether glassy or liquid, on other reactions is under study.